Metal Oxides Modified with Quantum Dots for Solar Generation of Hydrogen

A Synopsis of the proposed work to be carried out in pursuance of the requirement for the award of the degree

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Introduction

Hydrogen is widely considered to be an efficient energy carrier and the promising fuel of the future. It is the lightest element present in nature as its density in gaseous form at 1STP is 0.0838 kg/m^3 making it 14.6 times lighter than air (density is 1.225 kg/m^3) [23]. It contains a large amount of energy in its chemical bond as it shows the high energy to weight ratio (143 MJ/kg) in comparison to methanol (20 MJ/kg), diesel (46 MJ/kg) and gasoline (44 MJ/kg)[18] and pertain high heat of combustion (38 kcal/gm). Beside this Hydrogen is clean and environment friendly gas. Combining all of these properties of hydrogen makes it to show many potential applications, like the powering of nonpolluting vehicles, domestic heating, and aircraft etc. [3,25]. Furthermore, hydrogen has its own valuable right for its use as a basic chemical in petroleum refining and in ammonia synthesis [22]. However, Hydrogen is not a primary source of energy but it is an energy carrier as nature does not contain hydrogen in gaseous form but it can be extracted from several compounds, such as methane, methanol, higher hydrocarbons and most importantly, it is found in water [3]. Current hydrogen production relies primarily on methane steam reforming method [3]. As methane is extracted from fossil fuels and combustion of fossil fuels results in carbon (CO_2) emission and other forms of environmental contamination into our atmosphere which leads to global warming. Also limited number of fossil fuel resources with its rising cost emphasizes the multiple benefit of developing renewable hydrogen production [8]. In this context, significant efforts have been done to develop the methods for the generation of hydrogen, which is renewable, economically viable and non polluting. Most promising "holy grail" technology of hydrogen production is Photoelectrochemical (PEC) water splitting that uses sunlight [3,9]. Sun is the most generous renewable resource as Thomas Edison once said: "I'd put my money on the sun and solar energy. What a source of power! I hope we don't have to wait 'til oil and coal run out before we tackle that" [9]. One of the main advantages of PEC technology is the production of hydrogen and oxygen at separate electrodes which allows easy separation of these gases with no heavy energy penalty for post separation [18]. Another advantage is that it is economically viable as both water and sunlight are freely available. It is interesting to note that ~3.5 x 10^{13} L of water would be needed to store the energy that world

uses in 1 year (4.7×10^{20} J) in the form of hydrogen which corresponds to 0.01% of annual rain fall [18]. This technology also secures the credit of being eco-friendly technology as clean hydrogen and oxygen is produced with no other byproducts. The third advantage is its recyclability due to the production of water as the combustion byproduct [21]. In this context, next section will briefly present the basic principle of Photoelectrochemical (PEC) Hydrogen Production.

A. Photoelectrochemical (PEC) Hydrogen Production:

PEC is the solar to chemical energy conversion process that breaks apart water into hydrogen and oxygen gases using sunlight [25]. PEC water decomposition is carried out in a cell involving three electrodes immersed in an aqueous electrolyte, out of which at least one is made up of a semiconductor exposed to the light and able to absorb the light. There are three choices for organizing the photo-electrodes in PEC assembly which describe as follows [3]:

- photo-anode made of n-type semiconductor and cathode made of metal;
- photo-anode made of n-type semiconductor and photo-cathode made of p-type semiconductor;
- photo-cathode made of p-type semiconductor and anode made of metal.

PEC assembly made up of one semiconductor and one metal electrode will be adopted and used for discussion on basic principle of PEC splitting of water for generation of hydrogen. Principle governing the photoelectrochemical water decomposition is based on the light energy conversion into charge carriers which is used for water electrolysis. Operation of photoelectrochemical water decomposition includes several processes that occur within photo-electrode and at the photo-electrode-electrolyte interface which is explained as follows specifically for n-type photo-anode semiconductor [3,9]. First step is the harvesting of solar radiation by semiconducting photo-anode for their intrinsic ionization by photons that occur only if photon energy is equal to or larger than band gap of material to produce electronic charge carriers.

$$2h\upsilon \rightarrow 2e^{-} + 2h\cdot$$

These Photo-generated charge carriers must be separated and transported towards their respective electrodes before recombination. This separation is favored by electric field being generated across the space charge layer. These charge carriers must be extracted to perform the water-oxidation/hydrogen-reduction half-reactions. This extraction process is strongly affected

by poor energetic alignment or poor surface kinetics that results in energy loss to radiation or heat and recombination loss. At photo-anode, Oxygen evolution reaction (OER) takes place when adsorbed OH^- ions from solution react with the holes forming oxygen gas and water molecules. At the cathode (counter-electrode), the free electrons react with water molecules to accomplish hydrogen evolution reaction (HER) and produce OH^- ions. External circuit provides the path for flow of electrons from anode to cathode to carry out the HER for Hydrogen production. Set of half-reaction in alkaline media can be written as following [18]:

$$4h^{\bullet} + 4OH^- \rightarrow O_2 + 2H_2O \qquad E^o_{ox} = -0.401 \text{ V vs NHE} \qquad \ldots OER$$

$$4e^- + 4H_2O \rightarrow 2H_2 + 4OH^- \qquad E^o_{red} = -0.828 V \text{ vs NHE} \qquad \ldots HER$$

Overall reaction: $4h\upsilon + 2H_2O(liquid) \rightarrow O_2(gas) + 2H_2(gas)$

Both half-reactions must be sustained simultaneously, coupled by their exchange of electron in solid and ions in solution. Conversely, in p-type photocathode systems, hydrogen evolution occurs at the semiconductor surface while oxygen evolves at the counter electrode [3,9]. In this process, the gibbs free energy change for the conversion of one molecule of H_2O to H_2 and 1/2 O_2 under standard conditions is +237.2 kJ/mol, Since this change is positive, energy needs to be supplied to drive electrolysis process which is equivalent to its corresponding reversible potential V_{rev}=1.229 V per electron transferred [3,9].

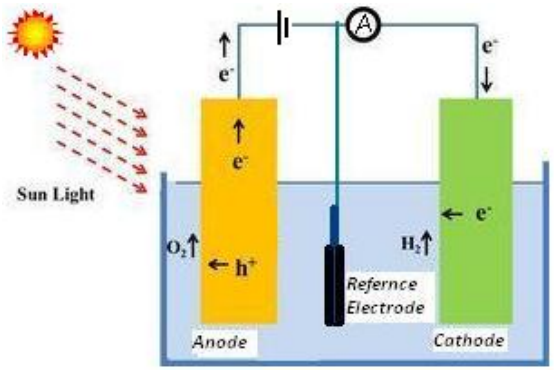

Figure 1: Systematic diagram of PEC cell

Under steady-state condition, this hydrogen producing performance of PEC system is directly related to photocurrent. As per HER reaction, production of one H_2 molecule require

consumption of two electrons thus hydrogen production rate is half of the flow rate of electrons i.e, half the photocurrent which is described according to following reaction:

$$R_{H_2} = \frac{I_{ph}}{2e} = \frac{(J_{ph} \times \text{Area})}{2e} \Rightarrow J_{ph} = \left(\frac{R_{H_2}}{\text{Area}}\right) \times 2e$$

where R_{H2} is the hydrogen production rate (s^{-1}), I_{ph} is the photocurrent (A), e is the electronic charge (C), Area is the illuminated photoelectrode area, J_{ph} is photocurrent density (A/m^2). Hence PEC-hydrogen production is effectively photocurrent density dependent phenomena i.e. more photocurrent density implies more hydrogen production rate.

B. Ideal Semiconductor for water splitting

Fujishima and Honda in 1972 presented a pioneering work [10] on the possibility of decomposition of water into hydrogen using TiO_2 semiconductor electrode. Several papers have been published in continuation to this work on performance of photo-electrochemical cells (PECs) using various materials as photo-electrode viz $SrTiO_3$, $BaTiO_3$, CdS, SnO_2, CuO, Fe_2O_3, GaAs etc [3]. But so far, no material has been identified to exhibit efficient splitting of water. Hence for commercialization of PEC technology, much R&D efforts are needed towards the development of various material processing technologies that has to be adopted to obtain high conversion efficiency. The material required for the photo-electrode in PEC should fulfill the following criteria:

i. Bandgap of material

Bandgap of the semiconductor plays a crucial role in the performance of photoelectrochemical water splitting. Theoretically, minimum amount of energy required to break apart the water molecules into hydrogen and oxygen is 1.23 eV, which decide the lowest limit of the material band gap [3]. But practically, splitting demands a potential of 1.8 eV, due to unavoidable losses in the cell. This energy corresponds to ~650nm of solar spectrum [9]. Thus semiconductor capable of splitting water should have a band gap greater than 1.8eV. On the other side**,** use of large band gap materials are limited due to their poor absorption property as below 400 nm the intensity of sunlight drops rapidly and hence obtained photocurrent is too low [21]. Therefore, band gap of the material lies in the range of 1.8 eV – 3.2 eV for efficient splitting of water in PEC system.

ii. **Band edges matching:** In order to have a successful water splitting reaction upon irradiation, the valence band(VB) of the semiconductor has to be located at a lower energy level than the chemical potential of O_2 evolution (H_2O/O_2) in solution with additional losses and the conduction band(CB) has to be positioned at a higher energy level than the chemical potential of H_2 evolution (H_2/H^+) with additional losses. This process facilitates the efficient charge transport at the semiconductor/electrolyte junction in PEC cell [3]. If the position of these energy bands does not fulfill the above specified criteria then an external bias (E_{bias}) has to be applied in order to induce the photo-oxidation process. However it is a matter of debate in the present scenario as it is recently reported that PEC water splitting is not sustainable even if band edges straddle the redox potential [9]. According to recent studies, under illumination condition, concept of quasi Fermi level has been introduced i.e. upon irradiation, equilibrium disturbed and the original single Fermi level splits into separate quasi-Fermi levels for electrons (F_e) and holes (F_h) and their separation determines the useable energy (Φ_{ph}) in the device [18] as shown in Figure 2. This is the energy which is capable of sustaining net PEC water splitting process which cannot be supplied by the internal energy in the bandgap, for example, in crystalline silicon, the bandgap energy is 1.1 eV while single-junction silicon solar cells have open-circuit voltages typically between 0.6 and 0.7V. It is reported that PEC-water splitting occur only when the electron potential at the counter-electrode, tied to the photoanode's back contact potential, is sufficiently high to drive the hydrogen-reduction half-reaction (including overpotential due to losses). Simultaneously, the quasi-Fermi hole energy (not the valance band energy of semiconductor!) at the solution interface is sufficiently low to drive water-oxidation (including overpotential due to losses). This concept may provide the useful insight for PEC system.

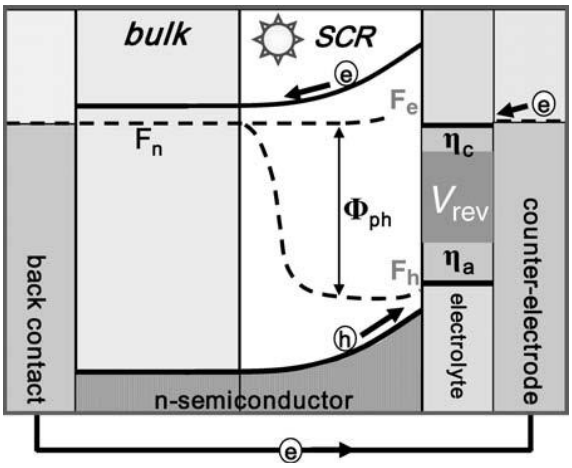

Figure 2: Band diagram of the photoanode PEC junction under solar illumination, illustrating the development of sufficient photopotential (i.e., quasi Fermi level split) to overcome the reversible potential plus the overpotentials for water splitting [9].

iii. **Low electrical resistance**: Energy loss by internal and external circuit resistance must be minimized in order to get efficient PEC water splitting. This energy loss mechanism includes electrode & electrolyte resistance, electrical lead and connection resistance, measuring and control equipment resistance. Semiconducting electrode possess larger resistance as compared to metal electrode which can be reduced by various surface engineering techniques like doping etc. [3].

iv. **High chemical stability**: In order to have a durable and long life PEC system for production of hydrogen, stability of the material in water is the critical issue. Electrochemical corrosion, photo corrosion and dissolution processes that take place at the semiconductor electrolyte interface lead to damage in the properties of photoelectrode. From this point of view, problems with most of the nonoxide semiconductors are either they undergo dissolution or form a thin oxide layer which prevents charge transfer across the semiconductor/electrolyte interface. On the other hand, oxide semiconductors are more stable, but they may be prone to decomposition [18]. So, these processes must be minimized in order to sustain high hydrogen production rates over long period [21].

v. **Low cost:** Material processing technology and material cost along with its consumption must be small enough for the commercialization of PEC technology. For healthy hydrogen economy, besides an efficient photoelectrode, electrode material must be abundantly available and should be environmentally safe.

Motivation

Main research in PEC technology is to find out/or modify a semiconductor material in order to get efficient splitting of water for production of hydrogen using solar energy. From this aspect, visible light absorbent materials used in photovoltaics should be suitable for PEC system as well. But, unfortunately the most promising material of photovoltaics is Si which is costly and also possesses insufficient value of band gap 1.1 eV to decompose water [24]. On the other hand most of the non-oxide semiconductors like GaP (E_g ~ 2.23 eV) and GaAs (E_g ~ 1.4 eV) are hardly attractive because of the scarcity of these materials as well as their unstablity in aqueous environment producing significant corrosion. [3, 24, 26]. Redox potentials for the decomposition reactions, of these non-oxide semiconductors generally lie within the band gap, leading to electrode photocorrosion [28]. In principle, stability is ensured when the oxidation decomposition potential of the semiconductor is more positive than the VB edge and the reduction decomposition potential lies more negative than the CB edge. Nevertheless, the most stable rocks and minerals that survive many years of weathering are all semiconducting oxide material. Many metal oxides have been examined in PEC generation of hydrogen since 1970's, but with very limited efficiencies. A general trend in the electronic structures of these oxides is that the valence band (VB) consists of O 2p orbitals, and the conduction band (CB) is formed by the valence orbitals of one or more metals. Due to this trend, especially in ionic crystals, the VB potential stays relatively unchanged at 3.0 ± 0.5 V vs NHE [28] for most metal oxides including TiO_2, $SrTiO_3$, WO_3, Fe_2O_3 and ZnO. On the other hand, metal ions either as dopant species or bulk matrix, could provide the aid in tuning the CB position and hence the band gap. Under illumination, minority carriers (holes) in the VB diffuse to the semiconductor-electrolyte interface to oxidize water (for n-type), but the disparity comes when the oxygen-centered VB at ~3.0 V and the OER potential at 1.23 V vs NHE present the wastage of extra 1.77eV energy by thermal relaxation [28]. From the band edge straddling point of view, first materials studied exhaustively were the perovskite structure oxides $SrTiO_3$ and $BaTiO_3$. On comparing, these materials with TiO_2, their conduction band edges are more negative than the water reduction potential thus better suited than TiO_2 for water photoelectrolysis. But, unfortunately, their band gaps are too large (including TiO_2) that they show very poor solar efficiencies [27]. One idea to both extends that increasing the spectral response of wideband gap oxide semiconductors

(WBGS) and to raise the valence band energy by incorporating sulphur, carbon or nitrogen into the lattice. A series of these compounds including $Sm_2Ti_2S_2O_5$, TaON, $Y_2Ta_2O_5N_2$, Ta_3N_5, and $LaTiO_2N$ as well as incorporating S, N or C into TiO_2 have been reported to produce H_2 and/or O_2 at quantum efficiencies of up to 30% [27], due to their smaller band gap, favouring band positions relative to the redox potentials of water. Unfortunately, most of these materials require sacrificial reagents to camouflage inherent oxidation or reduction decomposition reactions, thus show the same stability problems as the earlier materials [27]. Other possibilities of increasing the photo-response of wide bandgap semiconductors and to circumvent the problem with a low-lying valence band are doping of impurity ions, to introduce level within bandgap, surface-modification of the semiconductor by various surface treatments [3]. A variety of dopants viz Cr, Mn, V, Cu, Ni, Zn, Nb, Al, B etc introduced into these WBGS provided enhancement in photocurrent to some extend but observed photocurrents were much below the levels required for efficient PEC system [33]. Other Surface modification techniques of metal oxides are irradiation of swift heavy ion and deposition of metal dots [25], which are reported to be sometimes favorable towards PEC splitting of water. Niobium incorporated oxides like $NiNb_2O_6$, $ZnNb_2O_6$, Sr_2FeNbO_6, $K_2La_2Ti_{3-x}Nb_XO_{10}$ have also been studied with the aim of shrinking the large band gap to improve the solar response. [33]. On the other hand, smaller bandgap metal oxide semiconductors, viz WO_3, Fe_2O_3, NiO and Cu_2O harvest a larger percentage of the solar spectrum, but in general, their conduction band edge energies are often not optimally positioned for the production of hydrogen [28]. NiO (E_g ~ 1.4 eV) exhibits facile carrier recombination lead to smaller photocurrent, whereas CuO (E_g ~1.35eV) is reported to be photoelectrochemically unstable. The second insight is the high charge carrier mobility for efficient charge transfer. Mobility of charge carriers is related to the width of conduction and valence band i.e. broader bands, which are the consequence of more atomic wavefunctions overlap, could results in easy transport of free charge carriers in materials. Strongly curved wide bands indicate the high charge carrier mobility. A high mobility is especially desirable in photoelectrodes with indirect bandgap semiconductors like $YFeO_3$. Beside these some ternary oxides $FeTiO_3$(E_g ~2.16),$BaSnO_3$(E_g ~3 eV),$CdSnO_3$(E_g ~1.77eV),$CaTiO_3$(E_g ~3.6eV) etc have also been studied. Out of these some are unstable against photoelectrolysis like $FeTiO_3$ and some facing the problem of band edge stradding like $CdSnO_3$ [33]. Nevertheless, many colored composite oxides like $BiVO_4$ (E_g ~2.3 eV), $PbMo_{1-x}Cr_xO_4$ (E_g ~2.3 eV) composed of soft metal ions (e.g., Bi^{3+},

Pb^{2+}) have also been studied. Researchers are tirelessly working in this field to overcome the barriers [9]. After the exhaustive survey on PEC materials Fe_2O_3, TiO_2 and ZnO have been identified as interesting candidate for study due to their promising characteristics. Fe_2O_3 and related modified compounds shows huge potential in PEC splitting of water as they are abundantly available and stable; usually does not corrode in contact with most electrolytes, inexpensive and has a near-ideal bandgap (~2.1 eV) for PEC applications [3]. But small photocarrier lifetime and low conductivity accompanied with inefficient transport properties due to improper alignment of band edges with redox levels for hydrogen/oxygen evolution produces a hindrance to water splitting reaction. This can be improved by introduction of doping or by means of any kind of surface engineering [26]. In this field, despite of being a large band gap (~3eV) material, TiO_2 is most frequently studied material, due to its high corrosion resistance or long term chemical stability [3,12] along with its band edges that matches to the redox level of water, which facilitate easy transfer of charge carrier at semiconductor/electrolyte junction in PEC cell [26]. Another important candidate for PEC water splitting is ZnO (E_g ~ 3.3 eV) which has very similar physical properties & energy band structure to that of TiO_2, but has electron mobility higher by 2-3 orders of magnitude [30**]** as compared to TiO_2. ZnO offers potential in the field of PEC due to its many advantageous properties like high electron mobility, high conductivity in its doped form, abundant availability, short diffusion length for incident photon as compared to TiO_2 [4,14]. It has been reported to absorb visible light through various modification techniques. Since no single material photoelectrode has been found to split water using solar energy efficiently without corrosion, therefore, the research in this field is going on to find out a photo-electrode through various modification, which can split water efficiently.

In this context, material of interest for this thesis would be the old pillars of PEC study i.e. α-Fe_2O_3 ,TiO_2 and ZnO with modified improved PEC properties.

In past few decades, **Nanotechnology** has established its place in every branch of Science. Unique properties of nanomaterials make them successful candidate for their use in PEC cell. These properties are strongly dependent on their shape, structure and size. These properties in general are large aspect ratio that increases the specific surface area enhancing the charge transfer kinetics at semiconductor/electrolyte interface [18], outstanding mechanical strength with light weight and enhanced electrical properties [2]. Further, nanoscale sizes are comparable to scattering lengths of the carriers, which significantly reduce the scattering rate and increase

the carrier collection efficiency [34]. The explanation of change in these semiconductor properties lies in confinement effect. This effect is explained as confinement of electronic motion within potential barriers when dimensions of the confinement are less than their deBroglie wavelength [2]. With this view, the effective properties of various nanoarchitectures for PEC are described as follows: **Two-dimensional-Nanostructured-layered system** shows many advantages in PEC studies. First, increased absorption due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness. Secondly, recombination losses are greatly reduced because charge carriers will travel through a shorter path [13]. In this context, many papers have been reported on the synthesis of nanostructured thin films of different metal oxides include WO_3 , ZnO [32], Fe_2O_3 [17,25] , and more commonly, TiO_2 [31] showing enhanced photo-response. **One-dimensional ordered nanostructures** are expected to improve the electron diffusion length in films that will provide a direct conduction pathway for the easiest collection of carriers as a result of which, possibility of charge recombination reduces [14,18]. In this context, modification of wide band gap semiconductor (WBGS) with respect to shape and size is expected to provide enhanced performance of optoelectronic devices [6]. However, efficiency is limited due to insufficient surface area of 1D nanostructures [14]. Many papers have been reported on the fundamental PEC studies using 1D-nanostructured MO semiconductor materials viz TiO_2 [12], Fe_2O_3 [26,29], WO_3 [34] and ZnO [5,6] with improved photo-conductive properties over bulk counter parts.

Zero-dimensional (0-D) nanoarchitectures: Quantum dots

Due to uniquely tunable particle size, visible light absorbent quantum dots (QDs) modified with metal oxide especially wide band gap semiconductor could provide the enhancement in efficiency for their use in PECs. The admirable property of QDs for PEC is the multiple charge carrier generation from a single high-energy photon [6]. Increased surface area of visible light absorbing QDs facilitates the efficient absorption of the incoming solar radiation to produce more charge carriers [2]. It is expected that occurrence of quantum size effects i.e. reduction of the size of QDs are more helpful for PEC [21]. As the size of QDs decreases, band gap energy values increases which is expected to have favorable driving force for electrons injection from the conduction band (CB) of QDs into the CB of metal oxide like in Fe_2O_3 that in turn facilitate the hydrogen generation by decreasing the required bias potential [4,15,18]. CdS, CdSe, & CdTe are widely studied quantum dots which belong to II-IV compound semiconductors category.

These quantum dots in association with metal oxide thin films have been selected for the PhD work, as they are direct band gap semiconductors which show large absorption coefficient (two orders of magnitude) as compared to indirect band gap semiconductors [18]. Several papers have been reported the potential of these quantum dots in photovoltaic solar cells. Zhang Quanxin et al. fabricated CdS/CdSe sensitized solar cell and have used ZnO nanorod-templated method to prepare the TiO_2 nanotube (TNT) with subsequent deposition of CdS, CdSe QDs on the photoanodes through chemical bath deposition (CBD) technique. As a result of this work, 4.61% maximum efficiency has been found for CdSe/TNTs array. Khan M. Taukeer et al.[19] studied the effect of cadmium sulphide (CdS) doping in poly(3-hexylthiophene) (P3HT) and P3HT/PCBM polymer matrix for photovoltaic application and observed increment in efficiency from 0.45 to 0.87% after incorporation of CdS quantum dots. Chen Hao Ming et al 2010 examined the CdTe QDs and ZnO nanowires combination for efficient photoelectrochemical splitting of water and found maximum photoconversion efficiency of 1.83%. The paper also reported the good chemical stability of examined structure.

Thus, it has been observed that use of QDs with semiconductors shows good potential in enhancing the efficiency of photovoltaic solar cell. However, very few reports have been seen on QDs sensitized metal oxide films for PEC application, especially with respect to nanostructuring.

Motivated with the encouraging results on the use of QDs in solar photovoltaic cell, this thesis would be focused on a study of the QDs modified metal oxide nanostructured thin films for their photoelectrochemical applications in the direction of getting an economical, efficient PEC system for generation of hydrogen.

Proposed Objectives:

Thesis mainly would be aimed at the PEC studies of hybrid formed with various visible light absorbent quantum dots & metal oxide photo-anode

Steps to be followed to achieve the above specified aim would be as below:

STEP I: **Synthesis**:

a. To synthesize CdSe/CdS/CdTe quantum dots of various size.

b. To synthesize nanostructure ZnO / Fe_2O_3/ TiO_2 thin film.

c. To synthesize quantum dots modified metal oxide thin film.

- To synthesize Fe_2O_3:CdSe/ TiO_2:CdSe / ZnO:CdSe composite/sensitized thin films.
- To synthesize Fe_2O_3:CdS/ TiO_2:CdS / ZnO:CdS composite/ sensitized thin films.
- To synthesize Fe_2O_3:CdTe/ TiO_2:CdTe / ZnO:CdTe composite/sensitized thin films.

STEP II- Characterization: Thin film samples so prepared, before and after modification, would be characterized to find out the effect of quantum dot modification on metal oxide film:

- ✓ Surface Morphology
- ✓ Phase formation and particle size
- ✓ Optical Absorption and Bandgap Energy
- ✓ Thickness

STEP III- Photoelectrochemical studies with respect to Current-Voltage Characteristics under dark and illumination to determine:

- ❖ Photocurrent Density
- ❖ Nature of Charge carrier
- ❖ Resistivity

- ✓ Mott Schottky plot ($1/C^2$ vs V/SCE) for the determination of:
  - ❖ Flat band potential
  - ❖ Depletion layer width
  - ❖ Carrier density

STEP IV- The samples exhibiting better photoelectrochemical response would be finally employed in **PEC cell** for:

- ✓ Efficiency calculation of hydrogen production
- ✓ Collection and quantification of hydrogen evolved

Proposed Methodology:

Step I: Synthesis of material

a.) Preparation of Quantum dots

Quantum Dots would be synthesized by organometallic method which is known to provide the best quality QDs [1]. This method will be accomplished in two process: nucleation and growth of spherical nanoparticles synthesized in colloidal solutions

[7,11,15]. Growth time and temperature can vary to obtain different size of QDs with the hot injection technique in a non-coordinating solvent [11].

b.) Preparation of metal oxide nanostructure

Nanostructured thin film of hematite would be made from sol-gel method or electrochemical process [16,17]. ZnO rods would be grown in two step process: deposition of seed on the substrate and then growth of rod [4,5].

c.) Composite/sensetization of QDs with above prepared metal oxide would be done via simple dipping method.

Step II. Characterization of Material Prepared

a.) Surface Morphology

To investigate the structural properties of these nanostructures Transmission Electron Microscope (TEM) [at IITK], Atomic Force Microscopy (AFM) [at DEI] and Scanning Electron Microscopy (SEM) [at IITK] would be used. TEM would be employed for detection of as prepared QDs. AFM & SEM images would be used to determine surface roughness, grain size, grain structure and shape of the particle.

b.) Phase formation and Particle Size

X-ray diffraction would be carried out for the structural and phase analysis of the material prepared, using X-ray powder diffractometer [at DEI]. X-ray diffraction is a rapid analytical technique used to identify phase of the material, to check polycrystallinity of the compound formed and to confirm the presence of desired phase as a function of method of preparation. Particle size would also be calculated from XRD data using Scherrer's equation [18].

$$D = K\lambda_x / (\beta \cos\theta);$$

Where K is dimensionless constant, 2θ is the diffraction angle, λ_x is the wavelength of the X-ray radiation and β is the full width at half maxima (FWHM) of the XRD peak. FWHM of the peak is associated with the size of the particle; increase in FWHM is generally associated with decrease in particle size of the crystal. The larger the crystal size of a given component, the sharper would be the peaks on the XRD pattern for each crystal plane. The average particle size

of the crystal would be calculated by taking the average of particle size calculated from each peak of XRD pattern. Structure parameters like Lattice constant can also be calculated using peak positions of various planes. In the X-ray diffractogram different intensity peaks correspond to different (h k l) planes of diffraction. From intensity profile, generally with the highest intensity one can get the value of θ. Then with the knowledge of θ, λ and Miller indices of the said intensity peak, lattice parameter can be calculated.

c.) Optical absorption and Bandgap Energy

The band gap of the material has a crucial impact on the energy conversion of photons [3]. To investigate the band gap of the material, studies of its optical absorption become necessary for solar hydrogen production. UV Visible absorption of the material prepared would be recorded by using UV – VIS spectrophotometer [at DEI]. It can give the idea about light harvesting capacity of the material. The value of bandgap energy of the material would be calculated using the following equation [18,20]:

$$(\propto \boldsymbol{h\nu}) = \boldsymbol{A(h\nu - E_g)^n}$$

In this equation n is 0.5 for direct bandgap and 2 for indirect bandgap. Intercept of $(\alpha h\nu)^n$ vs $h\nu$ curve gives the bandgap of the material. Hence, α is the absorption coefficient near the absorption edge. A is constant, ν is the frequency, E_g is the bandgap of the material.

d.) Film Thickness

Thickness of the film is an important parameter in study of absorption of solar energy and thereby affecting the PEC response. Surface profilometer [at DEI] would be used for the thickness measurement of the film by alpha step (telestep) method. In this method, a fine needle (stylus) scans the surface of the film and records the thickness of the film, when it takes the step at the edge of the film. While depositing film on the substrate, a portion of the substrate area would be covered by scotch tape to obtain the sharp step edge of the film.

Step III. Photoelectrochemical Studies

Electrode Preparation

From the semiconductor thin film samples obtained in step I, electrodes would be fabricated by using silver paste and copper wire.

(i) Current – Voltage Characteristics

Quantum dots modified/unmodified metal oxide thin film electrode would be used in three electrode configured photoelectrochemical cell to observe its photoresponse. Current-voltage characteristics of the cell would be studied both under darkness and illumination. Electrolyte (in photoelectrochemical cell) of definite pH will be used for dipping these electrodes which will then be illuminated by an intense light source (UV-VIS) to observe the characteristics under light. The magnitude of photovoltage and photocurrent is expected to depend on the electrolyte, nature and amount of dopant, method of preparation of sample, film thickness, particle size etc.

(a) Photocurrent Density

Photocurrent density would be extracted from the current-voltage characteristics by subtracting dark current from the current under illumination, for unit area of all the samples. The photocurrent produced is an indirect measurement of hydrogen production.

(b) Nature of Charge Carrier

Current-Voltage characteristics of the semiconducting electrode in PEC cell would be used to differentiate the n or p type nature of the material in working condition.

(c) Resistivity

Current-Voltage (I-V) characteristics of the film in dark would be used for resistivity calculation. Resistance of the samples would be calculated from the slope of the current-voltage characteristics in linear region at large external bias of the semiconductor electrode in PEC cell. Resistivity calculation uses the following relation:

Resistivity (ρ) = (Resistance x Area) / thickness

(ii) Mott Schottky plot for determination of Flatband potential, Carrier concentration and Depletion layer width:

An LCR meter would be employed to measure capacitance at semiconductor/electrolyte junction. Flat band potential and carrier density can be calculated by $1/C^2$ versus electrode potential (V/SCE) plot (Mott Schottky plot) with the help of the following equation [18]:

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon_o \varepsilon N}\right)\left(V_{app} - V_{FB} - \frac{kT}{q}\right)$$

Here ε_o is the permittivity of the vacuum, N is the carrier density, V_{app} is the applied potential, ε is the dielectric constant of the semiconductor, $\frac{kT}{q}$ is the temperature dependent term, V_{FB} is the flat band potential and C is the capacitance. The intercept of linear plot at $C^{-2} = 0$ determine the flat band potential. The Flat band potential V_{FB} is the potential that has to be imposed on

electrode to make bands flat. The value of flat band potential reflects the thermodynamic ability of semiconductor to reduce water to hydrogen. The donor concentration N_D for n-type photo-anode material would be calculated from the slope of Mott-Schottky plot using the relation [17]:

$$\textbf{Slope} = 2/\varepsilon\varepsilon_0 qN$$

The depletion layer width (w) of semiconductore/electrolyte interface would be determined from capacitance measurement across the junction at zero applied voltage using the formula:

$$w = \varepsilon\varepsilon_0/C$$

Step IV: Efficiency calculation and quantification of hydrogen

i. Calculation of Efficiency

Ratio of usable chemical energy in the generated hydrogen gas to the total solar energy delivered to the system is called Solar-to-hydrogen conversion efficiency (STH). STH (η) of the photoelectrodes would be calculated from the photocurrent density upon illumination with light [9]. Following equation would be employed for the calculation of efficiency:

$$\eta(\%) = J_p\left[\left(1.23 - V_{app}\right)/I_o\right] \times 100$$

where J_p is the current density in mA/cm^2, I_o is the input intensity of incident light in mW/cm^2, $V_{app}=V_{mea}-V_{aoc}$, where V_{mea} is the electrode potential applied on working electrode at which photocurrent would be measured and V_{aoc} is the electrode potential of same electrode in open circuit condition.

ii. Collection and Quantification of Hydrogen

The electrodes with best photoresponse would be utilized for hydrogen production. In PEC cell, hydrogen production rates would be measured by collecting the gas liberated over cathode (for n-type semiconductor) within predefined duration with the help of inverted burette by downward displacement of water.

Literature Review:

Although, vast literature is available on the material study for PEC splitting of water, but this literature survey highlights the quantum dots modified metal oxide nanostructures in photoelectrochemical application. Given below is a review of some important reports published.

Fujishima and Honda (1972) in their pioneering work were the first to report the solar energy initiated photoelectrolysis of water using a single crystal of TiO_2 as the photoanode at which O_2 evolved. Electrons released

from anode travelled by a wire to Pt electrode, at which H_2 was evolved. The cell was chemically biased because the pH was different in cathodic and anodic compartment.

Grätzel Michael et al (2001) provided the historical background, and various developmental prospects for photoelectrochemical cells along with explanation of operational principle of photoelectrochemical cells based on n-type semiconductors. This paper put light on the processes that occur at semiconductor–electrolyte interface to explain PEC behavior through energy level diagram which showed the different states at junction like flat band potential state, accumulation layer state, depletion layer state and inversion layer. According to author, nanostructuring of the semiconductor introduces profound changes in its photoelectrochemical properties.

Bak T. et al (2002) outlined the requirements for photo-electrodes in terms of semiconducting and electrochemical properties that has to be fulfilled for efficient hydrogen, accompanied with material related issues. The paper also highlighted the general issues that have a great impact on the efficiency of photoelectrochemical cell. Authors have provided the useful data on the performance of photo-electrode(especially TiO2) sensitized through doping (Cr, Al etc.), noble metal particle(Ag,Pt etc) incorporation & dye deposition etc and gave the formation of electrochemical chain of PEC on the basis of band model representation.

Zhong Lin Wang et al (2004) have provided the detail discussion on ZnO nanostructures and solid–vapour process techniques for its synthesis. Authors have introduced us with morphological controlled different ZnO nanostructures like nanorod, nanobelts, ultranarrow nanobelts, hierarchical nanostructures, nanocombs, nanosaws, nanosprings and nanospirals seamless nanoring along with their detail. Paper also emphasized various properties of ZnO like luminescent property, tunable electrical properties, photoconductivity, thermal conductivity and piezoelectricity of the polar nanobelts along with their potential applications in gas chemical and biosensors, field effect transistor, nanoresonators, and in photoelectrochemistry.

Kumari Saroj et al (2006) communicated the paper on the PEC studies of Zn-doped Fe_2O_3 films synthesized by spray pyrolytic method by varying the different doping concentrations as 0.5, 1.0, 1.5, 5.0 and 10.0 at% and reported that Zn doped Fe_2O_3 samples yielded better photoresponse due to increased resistivity, increased flatband potential and decreased donor density. The optimal doping concentration was reported to be 5 at% which gave highest photocurrent density of ~0.64 mA cm^{-2} at an applied potential of 0.7 V/SCE. This was attributed to increase in flatband potential (negative) which helps in transfer of charge carriers at the interface, accompanied with increase in depletion layer width at the Junction that in turn increases the absorption of incident light energy.

Satsangi Vibha R. et al (2008) discussed the preparation of nanostructured thin film/pellets of Fe_2O_3 by spray pyrolysis and sol-gel method that were employed for investigation of photoelectrochemical response, before and after addition of various dopants. Paper reported that spray pyrolysis method exhibited better photoresponse as compared to sol–gel method for preparation of thin film. In this paper, surface of thin film was modified with Cu/Zn islands or irradiated by Swift ion and best photoresponse exhibited by 5.0 at% Zn doping. Authors have provided the possible explanation for this best response that annealing of Zn dotted islands could produce wide band gap ZnO, and behave like an efficient catalyst for the swift migration of the charge carriers.

Xunyu Yang et al.(2009) have reported the synthesis of nitrogen-doped zinc oxide (ZnO:N) nanowire arrays with controllable amount of nitrogen concentration for their use in photoelectrochemical hydrogen generation. Hydrothermal method was used for growth of vertically aligned ZnO nanowires, followed by incorporation of Nitrogen as a dopant through annealing in ammonia. ZnO:N nanowires i.e. N substitution at O site in ZnO nanowires is 3.7%

showed enhanced photoresponse as compared to pristine ZnO nanowires with overall hydrogen generation efficiency of 0.15%. This might be attributed to narrowing the effective bandgap of ZnO through N doping that substantially improves the light absorption capacity.

Chen Hao Ming et al (2010) have discussed the results of ZnO nanowires loaded with CdTe QDs for their use in PEC. Modified hydrothermal method was used for the growth of ZnO nanowires on FTO substrates and subsequently these nanowires are loaded with CdTe QDs for various deposition times. Authors have noticed very good stability of this structure by analyzing the photocurrent response in non sacrificial electrolyte which comes out to be identical after 50 cycles. To obtain exact efficiency, all PEC studies were carried out in a 0.5M aqueous solution of Na_2SO_4 without sacrificial reagents and appreciated maximum photoconversion efficiency of 1.83% after 24 h sensitization which is 200% more than that of pristine ZnO nanowires. According to this paper, highest achieved efficiency and stability can be attributed to fast & efficient transfer of the photogenerated electrons from CdTe to the ZnO nanowires and generation of multiple excitons from single photon using QDs.

Chouhan N.et al (2010) investigated the CdSe sensitized ZnO nanorods structure and the effect of annealing on it for their use in photoelectrochemical water splitting under visible light illumination. Aqueous solution growth method was used for synthesis of ZnO nanorods which include $Zn(acac)_2{\cdot}2H_2O$ for seeding of FTO substrate and aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ and hexamethylenetetramine for growth. In this paper, CdSe QDs were modified with ligand exchange (TOP to MPA) process, before loading as it improve the electron transfer rate. At zero applied bias, the maximum photocurrent density of 2.48 mA/cm^2 was observed for the annealed CdSe QD/ZnO NR arrays film. This result attributed to autoignition of linker 3-mercaptopropionic acid (MPA) at 350°C, which causes the reduction of number of defects as CdSe QDs settle down in free pores of ZnO.

Gao Xian-Feng et al (2010) have utilized the sequential chemical bath deposition method for sensitization of CdS and CdSe quatum dots on TiO_2 nanotube array film to observe its photoresponse. Under AM 1.5 G illumination, short circuit current density of 13.0 mA/cm^2 was observed with the TiO_2 /CdS/CdSe photoelectrode. This was attributed to enhanced visible light absorption and the CdS layer insertion between TiO_2 and CdSe. It provides a larger driving force for the transfer of photoexcited charge carriers as relative Fermi level positions of CdS and CdSe to TiO_2 greatly affect the photoactivity of the CdS/CdSe cosensitized TiO_2 NTs.

Khan M. Taukeer et al (2010) have demonstrated the doping effect of cadmium sulphide (CdS) quantum dots (QDs) in poly(3-hexylthiophene) (P3HT) polymer matrix for photovoltaic performance evaluation. Enhancement in the device power conversion efficiency of the solar cell from 0.45 to 0.87% was observed after incorporation of CdS QDs in the P3HT matrix which was explained on the basis of the formation of charge transfer complex (CTC) between the host (P3HT) and guest (CdS QDs).Enhanced device efficiency came from postproduction thermal annealing process which decrease the series resistance and improve the contact between the active layer and Al.

Kumar Praveen et al (2011) examined the Nanostructured hematite thin films doped with zirconium prepared by electrodeposition method for their use in photoelectrochemical (PEC) hydrogen generation. Various techniques like XRD, Raman, XPS, SEM and UV-visible spectroscopy have been used to characterize the thin film. They have varied the doping level of Zr as 1, 2, 5 & 10 at.% and found maximum photocurrent density of 2.1 mA/cm2 exhibited by 2.0 at.% Zr-doped sample at 0.6 V/SCE. Best PEC response exhibited by the samples was attributed to high donor density which in turn showed improve conductivity and most negative flatband potential as more negative value of the flatband potential facilitates the charge separation in PEC application

Chouhan Neelu et al (2011) have examined the CdSe sensitized ZnO nanotubes structure as photoelectrodes in photoelectrochemical (PEC) cells. In this paper, ZnO (0 h) grew as rods grew along the 002 plane on FTO and then subjected for hexagonal etching of NRs using NH_4OH for their gradual conversion into nanotubes of length ~5 μm. Photoresponses were measured under illumination by a 300W Xe light source (>420 nm) with an intensity of 100 mW/cm^2 and in aqueous solution of the hole scavenger– electrolyte 0.35 M Na_2S and 0.25 M K_2SO_3 (pH = 13.3) to suppress the photocorrosion of CdSe QDs. The observed photocurrent density of annealed CdSe sensitized samples of ZnO NRs (0 h cooling) and NTs (24 h cooling) were 2.1 mA/cm^2 and 5.10 mA/cm^2 at zero bias, respectively. ZnO NTs@CdSe(QDs) gave the ~2 times more photo response as compared to ZnO NRs@CdSe(QDs) which was attributed to increased surface area to volume ratio of ZnO and high compatibility between the energy band positions of tabular ZnO and CdSe.

Kevin Sivula et al (2011) described many ways of developing nanostructured Fe_2O_3 thin film of different morphology like electrochemical synthesis method, solution based colloidal method, spray pyrolysis method, Atmospheric pressure, chemical vapor deposition method etc that strongly affect the performance of hematite in PEC. Paper also reported the solution to the problem of majority carrier transport in hematite films when it has been created from the colloidal approach. So the solution is to use nanometer-sized rod or wire arrays. Authors also provided the overview on various properties of hematite like crystalline and magnetic structure, optoelectronic characteristics, carrier transport, photogenerated carrier lifetime and the challenges in using hematite for PEC water splitting.

Huy B. T et al (2011) have discussed the procedure for synthesis of CdS quantum dots of various sizes by wet chemistry & a bottom up technique and noticed that the role of ligands, chemical intermediates, nucleation temperature, grown temperature, speed of centrifugation, etc. strongly affect the quality of the nanocrystals. From this procedure obtained CdS QDs have the diameter lied in the range 3.8 – 4.5 nm with a narrow distribution when the nucleation and growth temperature was 290 and 260 ^oC, respectively. Authors have examined that the diameter of CdS QDs can be manipulated by changing parameters such as the growth temperature or the concentration of 1-octadecene. Decreased particle size and increased PL intensity was observed by increasing concentration of cadmium which lead to the appearance of more cationic monomers, that stop the nucleation process quickly. Paper has pointed out that excess of oleic acid might cause the cationic monomer excess or destroys CdS particles in the growth process of quantum dots.

Zhang Quanxin et al (2012) have reported the series of ordered photoanodic architectures (including ordered TiO_2 nanotube arrays (TNT), ZnO nanorods, ZnO/TiO_2 core/shell nanostructures) for CdS/CdSe sensitized solar cells (QDSCs). They were fabricated directly on transparent conductive oxide glasses by a facile sol–gel assisted template process. A promising light-to-electricity conversion efficiency of up to 4.61% has been achieved with 3 mm long $TiCl_4$ treated TNT arrays after optimal 14 hour QDs deposition time. Obviously, with increasing the CdSe deposition time, a greater amount of the CdSe QDs deposited on TNT arrays would generate more photo-excited electrons and reduce the recombination rate between photogenerated electrons and S_2^{2-} ions, thus gave higher efficiency of the device.

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